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(54) Activated biocidal compositions

(57) The capability of an organic peroxyacid to act as a broad spectrum biocide is boosted by incorporating an activating amount of a metal selected from iron and copper, thereby permitting a lower concentration or amount of the organic peroxyacid to be employed. Preferably, the compositions employed for this purpose exclude metal chelators. The compositions can be employed to treat a wide range of materials, including aqueous media, such as effluents and process waters, hard surfaces and growing or harvested plant materials. The peroxyacids include aliphatic peroxyacids such as peracetic acid and aromatic peroxyacids, possibly in salt form, such as magnesium monoperoxyphthalate. Other components which may be incorporated in the compositions include a bromide, iodide and/or alkyl sulphate surfactant which can likewise boost the biocidal performance of the organic peroxyacids.

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### Biocidal Compositions

The present invention relates to biocidal compositions and particularly to biocidal compositions containing an organic peroxyacid. The present invention further  
5 relates to the use of such compositions for disinfection or sanitisation.

Organic peroxyacids have been recognised, hitherto, as microbiocides having a wide spectrum of activity. Thus, the class of organic peroxyacid compounds or  
10 representative members of it has been proposed for action against a wide range of contaminating micro-organisms including bacteria, both gram +ve and gram -ve, yeasts, fungi, algae and viruses. Such peroxyacids include aliphatic peroxyacids such as peracetic acid and  
15 cycloaliphatic or aromatic peroxyacids such as monoperoxyphthalic acid, the latter of which can be employed advantageously in the form of its magnesium salt. Publications describing the biocidal properties of preformed peroxyacids include GB-A-2 137 882 and GB-A-  
20 2 207 354 and of peroxyacids generated in situ from precursor compounds in US-A-3 684 477.

It is continuing objective to find ways of improving or augmenting the effectiveness of biocides.

According to the present invention there are provided  
25 biocidal compositions comprising an organic peroxyacid and an activating amount of an iron or copper compound.

By the use of compositions according to the present invention, it is possible to either increase the biocidal capability of organic peroxyacids. The improvement can manifest itself in a number of ways. In one way, a  
5 faster rate of disinfection or sanitisation or the killing of a higher proportion of the undesired micro-organisms is obtained under selected conditions than — would be the case if the peroxyacid had not been activated. In a second way, a previously acceptable  
10 extent of disinfection or acceptable rate at which disinfection or sanitisation takes place is achieved using a lower amount or concentration of the organic peroxyacid or under less favourable conditions for disinfection. Naturally, the benefit can also be taken  
15 using an intermediate combination of the foregoing ways.

In the present invention, the effectiveness of the peroxyacid is enhanced by the addition of even a small relative amount of iron/copper compounds, which latter are sometimes referred to herein as metal activators.  
20 One convenient way of expressing the amounts of organic peroxyacid and iron/copper compounds employed in the compositions according to the present invention refers to the equivalent mole ratio of peroxyacid to metal activator. The equivalent number of moles of a  
25 peroxyacid is its actual number of moles multiplied by the number of peroxyacid groups within the molecule. It is often desirable to select the relative amount of metal activator such that its mole ratio to peroxyacid is at least 1:100 and in many instances is up to about 1:1. A  
30 convenient range of mole ratios is often from about 1:40 to 1:2. Such ranges of mole ratios can also be expressed as weight ratios, but it will be recognised that at any given weight ratio, the mole actual ratio will vary depending on the molecular weight of the  
35 selected organic peroxyacid and the selected metal salt. Accordingly, the weight ratio of metal salt to organic peroxyacid is in many instances selected in the range of

from about 5:1 to 1:375 and particularly from about 2.5:1 to about 180:1. If lower molecular peroxyacids such as aliphatic C2 to C4 peroxyacids are considered, the weight ratio of organic peroxyacid to metal quite often falls in the range of about 2.5:1 to about 1:50 and if a significantly heavier peracid is employed, for example substituted peroxybenzoic acids or monoperphthalic acid or a salt thereof, the weight ratio is often selected in the range of from 1:1 to about 1:180.

10 The organic peroxyacid can be any aliphatic, cycloaliphatic or aromatic peroxyacid. Suitable aliphatic peroxyacids include monoperoxyacids having the general formula  $R-CO_3H$  in which R represents an alkyl group, usually containing not more than about 12 carbons, often unbranched. Examples of such compounds include peracetic acid, perpropionic acid, perbutanoic acid, pernonanoic acid and perlauric acid (perdodecanoic acid.) The peroxyacid is often made by reaction between hydrogen peroxide and the corresponding carboxylic acid or acid anhydride. Such made peroxyacids can be separated from the reaction mixture before being incorporated in biocidal compositions. Alternatively, and especially for low weight peracids such as peracetic or perpropionic acid, it is often more convenient to employ the resultant reaction mixture which can contain some residual carboxylic acid and hydrogen peroxide, rather than distilling out the peroxyacid. Other suitable aliphatic peroxyacids contain two peroxyacids groups and can be represented by the formula  $HO_3C-R_A-CO_3H$  in which  $R_A$  often contains from 2 to about 12 carbons, in many instances in an unbranched chain.

Yet other suitable peroxyacids are aromatic or cycloaliphatic and can be represented by the formula  $HO_3C-R_X-A$ , in which  $R_X$  represents the aromatic or cycloaliphatic nucleus and A represents one or more substituents selected from hydrogen, alkyl, halo, sulpho, carboxyl or peroxycarboxyl groups. Optionally, the

sulpho, carboxyl and/or peroxy-carboxyl groups may be present as a salt, though preferably a magnesium salt for carboxyl and peroxy-carboxyl groups or preferably a potassium salt for sulpho groups. As a further option  
5 the peroxyacid molecule may contain one or more embedded amido or imido groups within its structure. Examples of aromatic peroxyacids include perbenzoic acid, t-butyl perbenzoic acid, p-chloroperbenzoic acid, mono or diperoxyphthalic acids including monoperorthophthalic  
10 acid, or preferably the magnesium salt thereof, and diperoxyphthalic acid, sulphoperbenzoic acid, preferably the potassium salt thereof, phthalimidoperalkanoic acids, alkylamidoperbenzoic acids and benzoamidoperalkanoic acids. A mixture of any two or more of the foregoing  
15 organic peroxyacids may be employed.

The metal activator can comprise any non-chelated iron or copper compound. Many suitable activators comprise salts of iron or copper, including in particular water-soluble salts. Both ferrous and ferric iron salts can be  
20 employed and the copper is normally employed as the cupric salt. Suitable salts include the salts of mineral acids including halides, and in particular bromide or iodide, and oxyhalides, sulphate, phosphate, including tripolyphosphate, tetrapyrophosphate and  
25 hexametaphosphate, nitrate, and salts of weak acids, such as carbonate and carboxylates like acetate.

However, it is preferable to exclude from the solution, those compounds which can chelate readily with iron or copper, such as aminopolycarboxylates (eg EDTA) or  
30 aminopolyphosphonates. In general the metal activator is a solid at ambient temperatures, and it is particularly suitable to employ it either in particulate form or in solution, often conveniently in water.

When both the organic peroxyacid and the metal  
35 activator are solid at normal storage temperatures, ie typically not higher than about 35 - 40°C, an especially suitable form of the composition comprises a particulate

mixture. Alternatively, the two components may be compressed together into a tablet, possibly after intermixing or possibly in layers of each component, generally after desensitisation to the extent needed to render the peroxyacid resistant to shock.

Optionally, the invention disinfectant or sanitising composition can also include diluents to aid dosing of suitable amounts of the active biocidal components at the point of use, and/or to improve the safety of the composition by controlling any residual tendency of the selected peroxyacid to decompose rapidly when subjected to impact or thermal shock. The diluent for solid peroxyacids may be incorporated as a particulate mixture, as a co-granulate, or as a coating agent. Many suitable diluents are alkali or alkaline earth metal salts of mineral acids, including in particular sodium and/or magnesium sulphate or alkali metal phosphates. Incorporation of a magnesium salt can be useful.

Such a mixture of solids has the advantage of being readily transportable and stored and of retaining the ratio of peroxyacid to metal activator within a desired range for a reasonable period of time. Indeed, by addition of a suitably selected amount of a phosphate salt, it is possible also to buffer aqueous media to be treated by the disinfection/sanitisation compositions at or around pH5, a pH at which excellent biocidal activity from the invention combination has been observed.

A further and often beneficial component of disinfectant compositions of the present invention can comprise a wetting agent, and in particular an anionic and/or possibly a nonionic surfactant. In most of the invention compositions, the proportion of surfactant is not greater than that of the organic peroxyacid, and in many instances, the surfactants constitute only a small fraction of the composition, for example in an amount of at least 0.1% w/w and often up to about 5% w/w for simple disinfection purposes. However, the amount may be

greater than that if the composition is intended for combined washing and disinfection, such as in sanitising nappies or the like, which can often contain up to as much as 30% surfactant(s) or sometimes even more. The  
5 choice of surfactant will take into account the physical state of the invention composition. Thus, when the invention composition is solid, the chosen surfactant would normally be selected from solid, often particulate or flaky materials, whereas if the composition is in  
10 liquid form then both the solid or lower weight, liquid surfactants can be used as well. It will be recognised that the presence of a surfactant will assist the cleansing performance of a biocidal composition, but it may improve upon, have little effect on or even impair  
15 the biocidal performance, depending upon which sub-class of surfactants is employed. This can be especially noticeable where the peroxyacid is employed at a concentration which by itself would be sub-lethal.

The range of surfactants which can be employed include  
20 conveniently the commonly available anionic surfactants containing a hydrophobic alkyl or fluorinated alkyl chain, typically containing on average about 12 or more carbons and a water-solubilising group such as a sulphonate, sulphate, carboxylate or phosphate group.  
25 Suitable classes of anionic surfactant include alkyl aryl sulphonates, especially dodecylbenzene sulphonate and the like, alkane sulphonates, olefine sulphates and sulphonates, sulphated alcohol ethoxylates, sulphated glycerides, alkyl-substituted sulpho-succinates, alkane  
30 sulphonates, alkyl phosphate esters, soaps, fluorinated alkyl or alkylbenzene sulphonates.

One further class of anionic surfactants and one which is of particular value in the context of disinfection or sanitisation using organic peroxyacids comprises alkyl  
35 sulphates, by which herein we mean the product obtained by sulphonating a fatty alcohol containing from about 9 to about 18 carbons, for example lauryl sulphate. Tests



have shown that this latter class of surfactants boosts biocidal activity of organic peroxyacids to a considerably greater extent than, for example, alkyl benzene sulphonate, so that incorporation of such a surfactant eg lauryl sulphate in the invention activated compositions in a suitable proportion such as from 0.2% to 2% w/w is preferred.

Particularly when the compositions are intended for washing purposes as well as disinfection, it can be considered desirable to incorporate at least one nonionic surfactant, often in an amount of up to 20% w/w of the composition, though it will be understood that the presence of a nonionic surfactant can impair to some extent the resultant biocidal capability of the composition. Suitable classes of nonionic surfactants include especially alcohol ethoxylates, alkyl phenol ethoxylates, and condensates of a polyethylene oxide and/or polypropylene glycol or of a polyhydroxy natural product such as sorbitol with a hydrophobic moiety, such as a fatty acid or fatty acid amide, or amine of similar alkyl chain length. Other nonionics include alkanolamides.

The invention compositions may contain additionally a bromide or iodide, often selected in a mole ratio to the organic peroxyacid of from 1:10 to 100:1 and in a number of instances from about 1:1 to about 10:1. In some instances it is convenient to incorporate the halide as an acid, alkali or alkaline earth metal salt and at least a proportion may be provided in the form of the iron or copper salt.

If the selected organic peroxyacid is itself a liquid at conventional storage temperatures, or has been rendered liquid by being incorporated into an aqueous or an alcoholic or aqueous alcoholic solution, it is preferable to make the composition shortly before it is employed, in that the presence of the iron and/or copper salts in intimate contact with the peroxyacid in a liquid

can accelerate the decomposition of the latter during prolonged storage, thereby reducing the effectiveness of the composition as a biocide.

For many applications, it is preferable to employ the invention compositions in a more dilute form than would be convenient for storage and/or transportation. Such dilution normally comprises the dissolution or suspension of the concentrate in water or an aqueous medium or less commonly in a non-aqueous medium such as a low molecular weight alcohol. In view of the aforementioned interaction between the peroxyacid and the activator in such liquid compositions, it is preferable to use the compositions shortly after their dilution, in order to maximise their effectiveness.

The invention compositions can be employed in a number of different ways, depending at least in part on the nature of that which it is desired to disinfect or sanitise. Thus, for example, if the compositions are disinfecting a liquid medium or a medium containing a substantial liquid fraction, the invention composition can be dosed in its concentrated form or optionally prediluted, the latter with the intention of assisting accurate dose control. On the other hand, if the compositions are being used to treat a disinfected solid surface or solid material, it is usually more convenient to first introduce at least some liquid into the composition if it is particulate mixture in order to improve contact between the active biocidal components and the solid/surface. For some purposes, such as in disinfecting and cleansing a hard surface, a paste or concentrated liquid form is often considered appropriate, the added liquid typically comprising from about half to about 5 times the weight of the solid composition before dilution. For use as a dipping bath or in the form of a spray, though, the extent of dilution is often from about 5 to about 100 fold. Such ranges are given only as guides and the extent of predilution is at the discretion

of the user, limited in practice by the desirability of retaining a sufficient concentration of components for disinfection to occur within a reasonable timescale.

Although the invention includes the use of copper salts, it is particularly suitable to select iron compounds, especially employed in or when the effluent from using the invention compositions is likely to be discharged into the environment, since iron compounds are as a general class much less toxic than copper compounds.

Some preferred compositions according to the present invention contain a halide such as bromide or iodide in addition to the metal and organic peroxyacid, which can be provided most conveniently by a suitable selection of the metal salt. Other preferred compositions contain additionally or alternatively an alkyl sulphate surfactant such as sodium lauryl sulphate. Yet further preferred compositions contain in addition to or instead of the halide and/or the surfactant a phosphate buffer in such an amount as to generate a pH of around pH5 in an aqueous solution at the point of use.

The present invention also includes as a second and closely related aspect a process for disinfecting or sanitising a contaminated substrate comprising the step of bringing the contaminated substrate into contact with an effective amount of a combination comprising an organic peroxyacid and an activating amount of an iron or copper compound.

In processes employing the invention combination, the two essential components may be employed in the form of a pre-prepared composition, for example a solid mixture or an aqueous or alcoholic solution or they may be brought together during the process itself, for example by separate introduction into a liquid substrate to be disinfected or by separate but simultaneous spraying onto a surface to be disinfected. The use of a pre-prepared mixture maximises the likelihood that that the two components will be employed in a particularly suitable

ratio, whereas separate but simultaneous employment minimises the risk of any deleterious interference between the components before they are brought into contact with the substrate for disinfection purposes.

5 In view of the diversity of substrates which can be disinfected, the concentration of each of the essential components can fall within very wide ranges. The concentration of the organic peroxyacid in an aqueous medium is desirably at least  $5 \times 10^{-5}$  M and in many  
10 embodiments is at least  $1 \times 10^{-4}$  M. In a number of processes, a concentration of less than  $10^{-3}$  M organic peroxyacid is employed, though as will be apparent from the preceding disclosures, concentrations of peracid in for example pastes or concentrated aqueous or alcoholic  
15 solutions of up to as high as 2 molar can be contemplated in some circumstances.

The concentration of metal salt activator employed in the process is desirably at least  $5 \times 10^{-6}$  M and is often at least  $10^{-5}$  M. In a number of suitable embodiments,  
20 the metal salt concentration is selected in the range of up to  $10^{-4}$  M, though as has been indicated hereinbefore, substantially higher concentrations of up to molar or greater can be contemplated.

From the foregoing, it will be seen that the invention  
25 contemplates in particular the addition of a low concentration of a metal salt to activate an organic peroxyacid, though in other circumstances higher concentration may be used, if desired. This is, of course, a concept diametrically opposed to the normal  
30 desire to separate organic peroxyacids from such metal salts or at the very least to chelate them so as to exclude or minimise peroxyacid decomposition.

The various organic peroxyacids and various metal salts which were described herein in the context of the  
35 invention compositions can likewise be employed in the invention process which similarly can also employ one or

more of the optional components, such as surfactant and phosphate pH buffer described herein.

The invention process can be carried out at the ambient temperature of the substrate, which will normally fall in the range of from about 0 to 35°C or where appropriate a higher temperature can be employed, such as by using a solution of the peroxyacid and metal salt which has been heated to a temperature of from about 35 to about 85°C.

The invention process is normally conducted at an acidic or approximately neutral pH and particularly at a pH in the region of about pH 3 to about pH7. In a number of preferred embodiments a pH of from about pH 4.5 to about pH6 is used, attained for example by a suitable introduction where necessary of alkali or acid into an aqueous medium to be treated or into the peroxyacid/metal activator disinfecting composition.

The invention process can be conducted for a wide range of substrates. Many of the treatable substrates are either liquid or solid. A contaminated gaseous substrate can be treated conveniently by spraying with a dilute solution of the invention biocidal combination or by bubbling the gas through a bath of the biocidal solution. One type of liquid substrate comprises micro-organism contaminated aqueous media such as recirculating process waters, or aqueous effluents prior to discharge. Such process waters occur in many different industries and can be contaminated by bacteria, algae, yeasts and more rarely by viruses. The broad spectrum activity of the organic peroxyacid is boosted by the metal activator and optionally by the halide and/or selected surfactant, if present. Without limiting to the following industries, contaminated process waters are prevalent during the processing of plant and animal materials, including the paper and pulp industries, the sugar refining industry, brewing, winemaking and alcohol distillating industries, effluents from straw treatments, discharges from sewage treatment works, including partially treated or merely

filtered discharges of sewage through pieplines extending out to sea, meat processing factories, carcass rendering activities and from the rearing of livestock. A further important source of contaminated aqueous media comprises  
5 cooling waters either industrially or arising from air conditioning units installed in large buildings, such as hotels, offices and hospitals.

The invention process can be employed to treat non-aqueous liquid media, such as cutting oils.

10 The invention process can be employed to disinfect solids, including hard surfaces, or contaminated articles intended for re-use in the food-rearing, horticulture, domestic or hospital environments. Hard surfaces can be made from metals, wood, ceramics, glass, and plastics and  
15 can include work-benches, walls, floors, sanitaryware, plant or apparatus, containers, tools, machinery, plant and pipework. It will be recognised that for such hard surfaces, it is often convenient to immerse smaller articles in a solution of the invention biocidal  
20 composition, and for larger applications, a spray or the like distribution means can be easier to employ. The process can also be contemplated for disinfecting water absorbent materials such as infected linen or especially soiled babies' nappies that are often made from terry  
25 towelling.

The invention compositions can be used to disinfect harvested plants or plant products including seeds, corms, tubers, fruit, and vegetables.

The contact period for the biocide and the contaminated  
30 substrate is often under the control of the process operator and in such circumstances, the concentrations of the biocidal composition is usually tailored to achieve the desired suppression of bio-activity in the contact time available. For recirculating waters, the effective  
35 contact periods can be very long, for example in excess of 24 hours whereas for effluents, holding tanks can be employed to ensure a suitable residence contact time

before discharge and dilution of the effluent.

Advantageously, in many instances, the invention process can be tailored by for example selecting appropriate concentrations of the active components of the biocide combination so as to achieve a very high kill of contaminant micro-organisms within at most 5 minutes, thereby keeping to a minimum the size of holding tanks and the like. For solid/surfaces, the biocide remains in contact until it ceases to have effect or is rinsed off.

In a further and related aspect of the present invention, the activated peroxyacid systems can be employed to treat growing plants selected from a wide range of crops, including cereals and meadowland, brassicas, legumes and root crops. Advantageously, the substantially enhanced biocidal activity caused by activating the peroxyacid with the metal salt, especially with the iron salt, and the concomitant reduction of peroxyacid concentration that is needed for disinfecting, is of particular value in the context of treating growing plants. It was recognised in EP-A-0 242 990 to Albright and Wilson that certain peroxyacids can be employed for the treatment of growing plants to control the growth of adventitious organisms acting as for example a fungicide. Peroxyacids if employed at too high a concentration can be phytotoxic, though the tolerance level for plants is not constant, so that the risk of a fungicidally effective, but phytotoxic treatment is reduced if the concentration of peroxyacid is lower. The Albright text indicates a peracid concentration of from  $10^{-3}$  M to 0.1 M.

In a particular variation of the present invention, there is contemplated a process for treating a growing plant with a broad spectrum biocide composition comprising a peroxyacid at a concentration of less than  $10^{-3}$  M containing a metal activator and especially iron at a concentration of at least  $10^{-6}$  M. By so doing, the peroxyacid is employed at a concentration at which it is

not effective by itself. Variations in the organic peroxyacids, metal activator compounds the concentrations of each, and the presence or otherwise of other permitted components of the biocidal treatment solution can be substantially as described hereinbefore with respect to the first aspect of the present invention, the composition itself, taking into account the limits imposed by the maximum peroxyacid concentration for plant treatments. It is particularly desirable to exclude metal chelators from the aqueous biocidal solutions containing the very low peroxyacid concentration.

In effect, in growing plant treatments, the capability of organic peroxyacid-containing compositions to act as a fungicide and as a bactericide is being harnessed, in order to counter, for example, rot, rust, blotch and black spot diseases resulting from infection by for example strains of Botrytis, Fusarium, Sclerotinia, Pseudocercoporella, Gaeumannomyces, Rhizoctonia and Pyrenophora.

In a variation of the invention, and particularly in a process for treating growing plants, there is employed as biocide a solution, conveniently an aqueous solution, of the organic peroxyacid at a concentration of from  $10^{-5}$  M to less than  $10^{-3}$  M together with an activating amount of a halide selected from bromide and iodide and/or an alkyl sulphate surfactant. The solution preferably has a pH of from about 4 to about 6. The amount of peroxyacid to employ can be regarded as a sub-lethal dose, were it to be employed by itself. Accordingly, in this aspect, in particular, the invention contemplates biocidal processes and compositions in which a sublethal peroxyacid is boosted by incorporation of selected activating materials.

The said activating amount of bromide or iodide is usually a concentration in an aqueous treating medium of at least  $10^{-5}$  M and often need not be greater than about  $10^{-3}$  M, ie is usually selected in substantially the same



range of concentrations as for the organic peroxyacid. The halide can be employed in the form of a salt having sufficient water solubility to deliver that low concentration of halide into solution. Suitable halides  
5 salts include alkali metal salts and iron or copper salts.

The activating amount of the alkyl sulphate surfactant often comprises a concentration of at least 0.1% by weight of the biocidal solution and particularly from 0.2  
10 to 1% by weight. A preferred alkyl sulphate is lauryl sulphate, typically in sodium salt form.

With appropriate variation in the components, the compositions of the variation can be produced and used by the methods described for making and using the metal  
15 activator-containing compositions.

Having described the invention in general terms, specific embodiments will now be described in greater detail, by way of example only.

Comparisons CA to CD, and Examples 1 to  
20 In these Examples and Comparisons, the biocidal activity each of the disinfectant systems was determined by the following general method. The variations in the systems are summarised in Table 1.

In each determination, a solution (8ml) containing an  
25 organic peroxyacid (magnesium monoperoxyphthalate hexahydrate, 187.5 mg/l of material having a peracid avox of approximately 5.4%) and optionally a metal salt in a concentration calculated to provide the desired concentration of metal after dilution of the solution to  
30 10ml) was warmed for 10 minutes to 30°C in a water bath. An inoculum (2ml, containing approximately  $5 \times 10^8$  cfu/ml of E. coli) was agitated vigorously with the aqueous disinfection solution at about 80 strokes/minute in the water bath, thereby forming a solution containing organic  
35 peroxyacid (MPPA) at a concentration of approximately  $4.5 \times 10^{-4}$  and bacterium at  $10^8$  cfu/ml.

After 4 minutes, an aliquot of 1 ml was withdrawn and any residual biocidal activity was neutralised with sodium thiosulphate, 0.5% w/v. After 10 minutes, a 1 ml aliquot of the mixture was serially diluted in dilute sodium sulphate solution (0.5% w/v) to a countable number of surviving cfus, of around 50 to 200. 1 ml aliquots of the diluted mixture were then transferred onto tryptane/soya agar (20 ml) in duplicate Petri dishes. The plates were incubated at 72 hours and the activity of each system observed.

Table 1

Comp/ Ex No	Metal ion conc $\times 10^{-6}$ M	% survival	Improved Kill Factor
15 CA	-	17.1	-
1	Cu 60	$<10^{-3}$	$>10^4$
2	Fe(II) 60	$<10^{-3}$	$>10^4$
3	Fe(III) 60	$<10^{-3}$	$>10^4$
CB	-	19.3	-
20 4	Fe(II) 5	0.58	33
5	" 4	1.75	11
6	" 1	3.83	5
7	" 0.5	9.0	2
CC	-	5.1	-
25 8	Fe(III) 20	$<10^{-3}$	$>5 \times 10^3$
9	" 15	$1.3 \times 10^{-3}$	$4 \times 10^3$
CD	-	0.5	-
10	Fe(III) 10	$2.0 \times 10^{-3}$	250
11	" 5	$8.9 \times 10^{-3}$	56

From the Table, it can be seen readily that addition of a low concentration of certain metal ions enhanced to a very significant extent the biocidal capability of the opragnic peroxyacid. Secondly, it can be seen that the extent of enhancement of activity varied in accordance with the concentration of the metal activator and that activation was especially apparent at metal ion concentrations of the order of about  $10^{-5}$  M or higher.

### Comparisons CE to CH, and Examples 12 to 16

These Examples and comparisons relate to compositions and biocidal treatments employing peroxyacids at a concentration of less than  $10^{-3}$  M together with a halide or surfactant activator. The procedure was the same as described for the preceding Examples and comparisons, and the variations are summarised in Table 2, below.

The abbreviation ABS indicates sodium dodecylbenzene sulphonate, the most widely employed anionic surfactant and SLS indicates sodium lauryl sulphate.

Table 2

Comp/ Ex No	Activator	conc % w/w	% survival	Improved Kill Factor
15 CE	-	-	14.8	-
CF	ABS	0.5	88.7	6x worse
12	SLS	0.5	$<10^{-3}$	$>14000$
CG	-	-	3.0	78
		$\times 10^{-4}$		
20 13	Br <sup>-</sup>	1.5	$<10^{-3}$	$>3000$
14	Br <sup>-</sup>	6	$<10^{-3}$	$>3000$
CH	-	-	5.5	-
15	I <sup>-</sup>	1.5	$<10^{-3}$	$>5500$
16	I <sup>-</sup>	6	$<10^{-3}$	$>5500$

From Table 2, it can be seen that incorporation of a low concentration of bromide or iodide together with a low and sub-lethal concentration of the organic peroxyacid was able to produce a combination having a very biocidal capability. Likewise the combination of the same level of organic peroxyacid with a dilute concentration of sodium lauryl sulphate transformed the biocidal capability of the organic peroxyacid very substantially. By comparison, the same concentration of sodium dodecyl benzene sulphonate, a compound which has already been proposed to stabilise peroxyacetic acid, resulted in the marked impairment of kill achieved.

## Claims:-

1. A biocidal composition comprising an organic peroxyacid and an activating amount of an iron or copper compound.
2. A composition according to either preceding claim characterised in that the organic peroxyacid is an aliphatic, cycloaliphatic or aromatic peroxyacid.
3. A composition according to claim 1 characterised in that the mole ratio of iron/copper activator to organic peroxyacid is selected in the range of from about 1:40 to about 1:2.
4. A composition according to any preceding claim characterised in that a metal chelator for iron or copper is excluded.
5. A composition according to any preceding claim characterised in that it contains at least 0.1% w/w of an alkyl sulphate surfactant.
6. A composition according to any preceding claim characterised in that it contains a bromide or iodide in a mole ratio to the organic peroxyacid in the range of from 1:1 to 1:10.
7. A process for disinfection or sanitisation in which a substrate to be disinfected is brought into contact with an organic peroxyacid, characterised in that the process employs together with the organic peroxyacid an activating amount of iron or copper.
8. A process for disinfection or sanitisation according to claim 7 characterised by employing a biocidal composition as such or after dilution substantially as described in any one of claims 2 to 6.

9. A process according to claim 7 or 8 characterised in that the organic peroxyacid is employed at a concentration selected in the range of from  $10^{-5}$  M to less than  $10^{-3}$  M.
10. A process according to claim 7 or 8 characterised in that the organic peroxyacid is employed at a concentration which in the absence of an activator is sub-lethal.
11. A process according to claim 9 or 10 characterised in that the process treats growing plants.
12. In a modification, a biocidal composition or process for disinfection or sanitisation, particularly for treating growing plants, characterised by employing as biocide a solution, preferably aqueous, of an organic peroxyacid at a concentration of from  $10^{-5}$  M to less than  $10^{-3}$  M together with an activating amount of a halide selected from bromide and iodide and/or an alkyl sulphate surfactant.
13. A composition or process according to any one of claims 7 to 12 characterised by employing bromide or iodide at a concentration selected in the range of from about  $10^{-5}$  M to about  $10^{-3}$  M.
14. A composition or process according to any one of claims 7 to 13 characterised by employing an alkyl sulphate surfactant at a concentration of from 0.1 to 1% w/w.
15. A composition or process characterised by having a pH of from about 4.5 to about 6.
16. A biocidal composition or a process for disinfection or sanitisation substantially as described herein with respect to any one Example.

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17.A biocidal composition or a process for disinfection or sanitisation substantially as described herein with respect to any novel feature or novel combination of features.